

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>5</sup> :</b> <b>C08K 7/00 // C08K 3/34</b> <b>C08K 9/06</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 93/11190</b> <b>(43) International Publication Date:</b> 10 June 1993 (10.06.93)
<b>(21) International Application Number:</b> PCT/US92/10098 <b>(22) International Filing Date:</b> 23 November 1992 (23.11.92)  <b>(30) Priority data:</b> 798,440 26 November 1991 (26.11.91) US  <b>(71) Applicant:</b> ALLIED-SIGNAL INC. [US/US]; 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07962-2245 (US).  <b>(72) Inventors:</b> MAXFIELD, MacRae ; 1226 Cambridge Avenue, Plainfield, NJ 07062 (US). CHRISTIANI, Brian, R. ; 139 Indiana Street, Maplewood, NJ 07040 (US).  <b>(74) Agent:</b> ROONEY, Gerard, P.; Allied-Signal Inc., 101 Columbia Road, P.O. Box 2245, Morristown, NJ 07962-2245 (US).		<b>(81) Designated States:</b> JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> POLYMER NANOCOMPOSITES FORMED BY MELT PROCESSING OF A POLYMER AND AN EXFOLIATED LAYERED MATERIAL DERIVATIZED WITH REACTIVE ORGANO SILANES  <b>(57) Abstract</b> <p>This invention relates to a process of forming a composite material comprising a continuous polymeric phase formed from a melt processible polymer and platelet particles having an average thickness equal to or less than about 50 Å, and a maximum thickness of about 100 Å and a reactive organic silane residue having a moiety bonded to the surface of said platelets and a moiety bonded to a polymeric phase, the composite material formed by said process and articles of manufacture formed from the composite material.</p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NL	Netherlands
BE	Belgium	GN	Guinea	NO	Norway
BF	Burkina Faso	GR	Greece	NZ	New Zealand
BG	Bulgaria	HU	Hungary	PL	Poland
BJ	Benin	IE	Ireland	PT	Portugal
BR	Brazil	IT	Italy	RO	Romania
CA	Canada	JP	Japan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SK	Slovak Republic
CI	Côte d'Ivoire	LI	Liechtenstein	SN	Senegal
CM	Cameroon	LK	Sri Lanka	SU	Soviet Union
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	MC	Monaco	TG	Togo
DE	Germany	MG	Madagascar	UA	Ukraine
DK	Denmark	ML	Mali	US	United States of America
ES	Spain	MN	Mongolia	VN	Viet Nam
FI	Finland				

- 1 -

POLYMER NANOCOMPOSITES FORMED BY MELT PROCESSING  
OF A POLYMER AND AN EXFOLIATED LAYERED MATERIAL  
DERIVATIZED WITH REACTIVE ORGANO SILANES

5

BACKGROUND OF INVENTION

1. Field of the Invention

This invention relates to a process for forming a  
10 composite material comprising a polymer matrix having  
dispersed therein platelet particles, derived from  
swellable intercalated layered materials derivatized  
with reactive organosilane compounds, and to composite  
materials formed by the process of this invention.  
15 More particularly, this invention relates to such a  
process where the intercalated layered material has  
layers which are compatible with the polymer of the  
matrix, such that during the process the polymer-  
compatible layers of the intercalated material  
20 dissociate one from the other to form platelet fillers.

2. Prior Art

A specific category of polymer composites has been  
described as a composite material comprising a polymer  
25 matrix having uniformly dispersed therein layers of  
silicate. Such nanocomposites are described in US Pat  
Nos. 4,739,007; 4,618,528; 4,528,235; 4,874,728;  
2,531,396 and 4,810,734; Deutsches Pat. 3808623 A1;  
Japanese Patent J 02 208358 A; EPA 0,398,551,  
30 0,358,415, 0,352,042 and 0,398,551; and technical  
publications by the patentees (J. Inclusion Phenomena  
5, (1987), 473-483; Clay Minerals, 23, (1988), 27;  
Polym. Preprints, 32, (April 1991), 65-66; Polym.

- 2 -

Prints, 28, (August 1987), 447-448; and Japan Kokai 76,109,998.

#### SUMMARY OF THE INVENTION

5        This invention relates to a process for forming a polymeric composite which comprises platelet particles dispersed in a polymeric matrix which comprises the steps of:

10        (a) forming a "flowable mixture" comprising a melt-processible polymer and a swellable and polymer-compatible intercalated layered material comprising layers having reactive organo silane species covalently bonded to their surfaces said species being compatible with said polymer and are reactive with said polymer  
15        under process conditions to form covalent bonds thereto; and

20        (b) subjecting said mixture to a shear having a shear rate which is sufficient to dissociate all or a portion of said layers one from the other to form platelet particles having an average thickness equal to or less than about 50 Å, and preferably having a maximum thickness of 100 Å, and to uniformly disperse said platelet particles in said polymer to form said polymer composite.

25        Another aspect of this invention relates to a composite material comprising a polymeric matrix which comprises a melt processible polymer having uniformly dispersed therein platelet particles having an average thickness equal to or less than about 50 Å and  
30        preferably having a maximum thickness equal to or less than about 100 Å, said material further comprising an organosilane species covalently bonded to a surface of said particles and covalently bonded to a polymer in said polymeric matrix.

- 3 -

The polymeric compositions of this invention exhibit one or more advantages over prior art composites as for example those described in U.S. Patent Nos. 4,739,007; 2,531,396 and 4,410,734; 5 Deutsches Pat. 3,808,623 A1; Japanese Patent No. 02 208358A and EPA 0,398,551; 0,358,415; 0,352,042 and 0,398,551. For example, the composite of this invention exhibits improved properties such as yield strength in the presence of polar solvents such as 10 water, methanol, ethanol and the like. Other advantages include enhanced heat resistance and enhanced impact strength. They also exhibit superior resistance to diffusion of polar liquids and of gases in the pressure of polar media. In addition, they 15 exhibit superior ability to fix dyes.

DESCRIPTION OF THE PREFERRED EMBODIMENTS  
OF THE INVENTION

The first step of this invention comprises forming 20 a "flowable mixture" comprising one or more polymers in a "polymer melt" and at least one "swellable and polymer-compatible intercalated layered material" which comprises polymer-compatible and reactive layers that are compatible and reactive with at least one of said 25 polymers. As used herein, a "flowable mixture" is a mixture which is capable of flowing at the submicron scale so that the layered materials may exfoliate into platelet particles comprising individual or a small multiple of layers, which may in turn disperse within 30 the polymer mixture. As used herein, a "polymer melt" is a melt processible polymer or mixture of polymers which has been heated to a temperature sufficiently high to produce a viscosity low enough for submicron scale mixing to occur. Temperatures used in the first 35 step are not critical and can be varied widely as

- 4 -

desired provided that the polymer employed is in the state of a polymer melt. In the preferred embodiments of the invention, process temperature should be at least as high as the melting point of the particular  
5 polymer employed, and below the degradation temperature of the polymer. In the more preferred embodiments of this invention, where the polymer is a thermoplastic polymer, the process temperature is such that the polymer will remain in the polymer melt during the  
10 conduct of the process. In the case of a crystalline thermoplastic polymers, the temperature is above the polymer's melting temperature. For example, a typical nylon 6 having a melting point of about 225°C can be melted in an extruder at any temperature equal to or  
15 greater than about 225°C, as for example between about 225°C and about 325°C. For nylon 6, a temperature of preferably from about 250°C to about 260°C is normally employed. In the cases of amorphous thermoplastics and vulcanizable rubbers, it is a temperature at which the  
20 viscosity is sufficiently low that processing of the polymer can be performed by conventional means.

The manner in which the flowable mixture is formed is not critical and conventional methods can be employed. For example, the flowable mixture can be  
25 prepared through use of conventional polymer and additive blending means, in which the polymer is heated to a temperature sufficient to form a polymer melt and combined with the desired amount of the intercalated layered material in a granulated or powdered form in a  
30 suitable mixer, as for example an extruder, a Banbury Mixer, a Brabender mixer, a continuous mixer and the like. The polymer melt containing nano-dispersed delaminated layered material may also be formed by reactive extrusion in which the layered material is  
35 initially dispersed as aggregates or at the nanoscale

- 5 -

in a liquid or solid monomer and this monomer is subsequently polymerized in an extruder or the like. Such monomer or other reactive solid or liquid dispersion can be injected into a polymer melt  
5 containing one or more polymers in an extruder or other mixing device. The injected liquid may result in new polymer or in chain extension or grafting to the polymer initially in the melt. Alternatively, the polymer may be granulated and dry mixed with the  
10 intercalated layered material, and thereafter, the composition may be heated in a mixer until the polymer is melted forming the flowable mixture. As described above, the flowable mixture is, in the second step, subjected to a shear in a mixer sufficient to form the  
15 dispersed nanocomposite structure of platelet particles in the polymer melt, and it is thereafter cooled.

Best results are generally obtained when the flowable mixture includes as little water as possible in order to avoid hydrolytic cleavage of the polymer  
20 and/or generation of void defects. Some polymers such as polyolefins can tolerate more than about 0.25% water by weight during melt processing, while others (such as condensation polymers as for example polyamides and polyesters) may be degraded if processed with water  
25 content greater than about 0.1% by weight. Consequently, in the most preferred embodiments, both the polymer and the intercalated layered material are rigorously dried and contain substantially no water. Ideally, the intercalated layered material is free of  
30 water that can be desorbed at temperatures up to the processing temperature. However, good results can be obtained when the intercalated layered material contains as much as about 2% by weight water and comprises less than about 5% by weight of the flowable  
35 mixture. For compounding with condensation polymers,

- 6 -

the intercalated layered material preferably contains less than about 1% by weight, more preferably less than about 0.5% by weight water and most preferably less than about 0.25% by weight water.

5 As a first essential ingredient, the flowable mixture includes a "swellable and polymer-compatible reactive intercalated material". As used herein, a "swellable and polymer-compatible reactive intercalated layered material" is a swellable layered material which  
10 as been intercalated by a neutral or ionic intercalant or intercalants comprising one or more reactive organo silanes compounds. The organo silane compounds are critical and have moieties that are reactive with the surfaces of the layers of the layered material and with  
15 one or more polymers in the matrix. These compounds function as reactive swelling/compatibilizing agent which act to weaken the interlayer cohesive energy by swelling the interlayer distances and increase the compatibility and bonding of the layers with the  
20 polymer melt by having covalent bonds with both the layers and the polymer.

Swellable layered materials are materials comprising planar layers arrayed in a coherent, coplanar structure between the intercalant or  
25 intercalants and a layer surface, where the bonding within the layers, is stronger than the bonding between the layers such that the materials exhibit increased interlayer spacing in their intercalation compounds. The intercalants or intercalants may be introduced into  
30 the interlayer spaces by either insertion, in the case of neutral molecules, or ion exchange, in the case of ions. The intercalants may be introduced in the form of a solid, liquid, gas, or solute. The intercalants may be introduced into the spaces between every layer,  
35 nearly every layer, or a large fraction (greater than



- 7 -

about 75%) of the layers of the layered material such that the resulting platelet particles comprise less than about 10 layers in thickness. The platelet particles are preferably less than about 8 layers in thickness, more preferably less than about 5 layers in thickness, and most preferably, about 1 or 2 layers in thickness.

Any swellable layered material having the above referenced characteristics may be used in the practice of this invention. Useful swellable layered materials include phyllosilicates. Illustrative of such materials are smectite clay minerals such as montmorillonite, nontronite, beidellite, volkonskoite, hectorite, saponite, sauconite, magadiite, and kenyaite; vermiculite; and the like. Other useful layered materials include illite minerals such as ledikite and admixtures of illites with the clay minerals named above. Other useful layered materials, particularly useful with anionic polymers, are the layered double hydroxides, such as  $\text{Mg}_6\text{Al}_3(\text{OH})_{18}(\text{CO}_3)_{1.7} \cdot \text{H}_2\text{O}$  (see W.T. Reichle, J. Catal., 94 (12985) 547), which have positively charged layers and exchangeable anions in the interlayer spaces. Other layered materials having little or no charge on the layers may be useful in this invention provided they can be intercalated with swelling agents which expand their interlayer spacing. Such materials include chlorides such as  $\text{ReCl}_3$  and  $\text{FeOCl}$ , chalcogenides such as  $\text{TiS}_2$ ,  $\text{MoS}_2$ , and  $\text{MoS}_3$ , cyanides such as  $\text{Ni}(\text{CN})_2$ , and oxides such as  $\text{H}_2\text{Si}_2\text{O}_5$ ,  $\text{V}_6\text{O}_{13}$ ,  $\text{HTiNbO}_5$ ,  $\text{Cr}_{0.5}\text{V}_{0.5}\text{S}_2$ ,  $\text{W}_{0.2}\text{V}_{2.8}\text{O}_7$ ,  $\text{Cr}_3\text{O}_8$ ,  $\text{MoO}_3(\text{OH})_2$ ,  $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{CaPO}_4\text{CH}_3 \cdot \text{H}_2\text{O}$ ,  $\text{MnHAsO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{Ag}_6\text{Mo}_{10}\text{O}_{33}$ , and the like.

Preferred swellable layered materials are those having charges on the layers and exchangeable ions such as sodium cations, quaternary ammonium cations, calcium

- 8 -

cations and the like between the layers which can be intercalated by useful reactive organosilane compound by an ion exchange mechanism. More preferred layered materials are those having negative charges or basic sites on the layers, preferably at least about 20 basic sites per 100 g of material, more preferably at least about 50 basic sites per 100 g of material and most preferably from about 50 to about 120 basic sites per 100 g of material. Most preferred swellable layered materials are phyllosilicates having a negative charge on the layers ranging from about 0.2 to about 0.9 charges per formula unit and a commensurate number of exchangeable cations in the interlayer spaces. Particularly preferred layered materials are smectite clay minerals such as montmorillonite, nontronite, beidellite, volkonskoite, hectorite, saponite, sauconite, magadiite, and kenyaite, with hectorite and montmorillonite having from about 20 basic sites to about 150 basic sites per 100 g material being the layered material of choice.

The interlayer spacing of the swellable/compatibilized layered material is critical and exfoliation must be sufficient large to allow for the desired dispersion of the layers during the process. As used herein, the "inter-layer spacing" refers to the distance between the faces of the layers as they are assembled in the intercalated material before any delamination (or exfoliation) takes place. The preferred clay materials generally include interlayer or exchangeable cations such as  $\text{Na}^+$ ,  $\text{Ca}^{+2}$ ,  $\text{K}^+$ ,  $\text{Mg}^{+2}$  and the like. In this state, these materials do not delaminate in host polymer melts regardless of mixing, because their interlayer spacings are usually equal to or less than about 4 Å. Consequently, the interlayer cohesive energy is relatively strong.

- 9 -

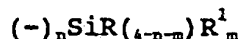
Moreover, the metal cations do not aid compatibility between and are not reactive with the surface of the layers and the polymer melt. On treatment with a suitable reactive organosilane compound of sufficient size, these layered materials are intercalated by the organosilane compound which reacts with the surfaces of the layered materials forming covalent bonds therein to increase interlayer distances to the desired extent. In general, the interlayer distance should be greater than about 4 Å, as determined by x-ray diffraction, in order to facilitate delamination of the layered material at the nanoscale. In the preferred embodiments of the invention, the interlayer distance is at least about 8 Å and more preferred interlayer distances are at least about 15 Å.

In order to facilitate delamination of layered materials into platelet particles and prevent reaggregation of the particles, these layers are intercalated with swelling/compatibilizing agents comprising one or more reactive organo silane compounds which bonds to the surface of the layers and which contains one or more moieties which can form covalent bonds with the polymer under process conditions. The reactive organo silane swelling/compatibilizing agents include a moiety or moieties which react with the surface of the layers displacing, totally or in part, the original ions and which bonds to the surface of the layers by way of one or more Si-O bonds which function as covalent bonds. The reactive organic silane compounds remain bonded to the surface of the layers during and after melt processing as a distinct interphase that is different from the bulk of the matrix polymer. The reactive organo silane swelling/compatibilizing agents also include a moiety or moieties whose cohesive energies are sufficiently

- 10 -

similar to that of the polymer that the surface of the platelets is made more compatible with at least one polymer, thereby enhancing the homogeneity of the dispersion in the polymeric matrix and which react with the polymer forming the matrix to form covalent bonds between the agent and the polymer during melt processing such that the layered material, which are essentially covalently bonded to the organo silane swelling/compatibilizing agent, becomes covalently bonded to the polymer. As used herein "compatible" refers to the extent to which the polymer matrix and the surface coating on the platelet particles (the compatibilizing agent) have a favorable interaction which promotes the intermingling of the matrix polymer and the surface layer in the interphase region. Compatibility derives from one or more of the following criteria: similar cohesive energy densities for the polymer and the derivatized platelets, similar or complimentary capacities for dispersive, polar, or hydrogen bonding interactions, or other specific interactions, such as acid/base or Lewis-acid/Lewis-base interactions. Compatibilization will lead to an improved dispersion of the platelet particles in the matrix and an improved percentage of delaminated platelets with a thickness of less than 50 Å.

The swelling/compatibilizing reactive agents comprise organo silane compounds which are covalently bonded to the layers and which include functional groups which are reactive and compatible with the polymer forming the polymer matrix. Illustrative of such compounds useful in the practice of this invention are silane agents of the formula:



where (-) is a covalent bond to the surface of the layer, m is 0, 1 or 2; n is 1, 2 or 3 with the proviso

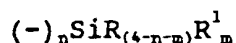
- 11 -

that the sum of m and n is equal to 3; R<sup>1</sup> is a non-hydrolyzable organic radical and is not displaceable during the formation of the composite; R is the same or different at each occurrence and is an organic which is bonded to the Si atom, and radical which is not hydrolyzable and displaceable during the formation of the composite which is reactive with the polymer matrix or at least one polymeric component of the polymer matrix to form covalent bonds between the reaction residue of R and the polymer and with the further proviso that at least one R group is compatible with such matrix.

Illustrative of useful R<sup>1</sup> groups are alkyl, alkoxyalkyl, alkylaryl, arylalkyl, alkoxyaryl and the like. Preferred R<sup>1</sup> groups are alkyl groups, more preferred R<sup>1</sup> groups are alkyl having from 1 to about 4 carbon atoms and most preferred R<sup>1</sup> groups are methyl and ethyl.

R groups are critical to the invention. R is apolymeric, oligomeric or monomeric radical having any number of carbon atoms which is selected from the group consisting of organic radicals which are compatible with the polymer forming the composite and which has substituents which are reactive with the polymer such as nucleophilic or electrophilic moieties which are capable of electrophilic or nucleophilic displacement reactions, coupling reactions varying opening reactions and the like as for example amino, carboxy, acylhalide, acyloxy, hydroxy, isocyanato ureido, halo, epoxy, epichlorohydrin and the like.

In the preferred embodiments of the invention silane agents are the formula:



wherein:

- 12 -

(-) is a covalent bond between the silicon atom and the surface of the platelet;

$R^1$  is alkyl, cycloalkyl, alkoxyalkyl, phenyl, phenylalkyl, alkoxyphenyl and alkylphenyl;

5  $R$  is an organic radical having at least one functional group which is capable of reacting with one or more polymeric components of the polymeric matrix to form covalent bonds, which radical may optionally include one or more heteroatoms or carbonyl atoms;

10  $m$  is 0, 1 or 2; and

$n$  is 1, 2 or 3 with the proviso that the sum of  $m$  and  $n$  is equal to 3.

In the more preferred embodiments of the invention the silane agents are of the above formula in which:

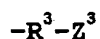
15 (-) is a covalent bond between the silicon atom and the surface of the platelet;

$-R_1$  is alkyl preferably alkyl or from 1 to about 4 carbon atoms, and more preferred methyl or ethyl;

$m$  is 0 or 1;

20  $n$  is 2 or 3; and

$-R$  is an aromatic or a aliphatic radical of the formula:

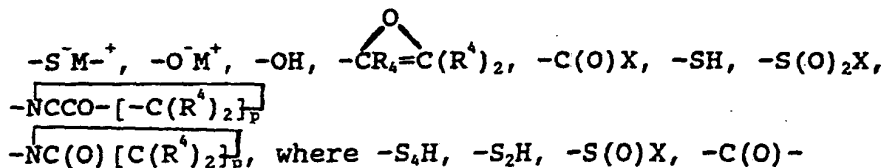


25 wherein:

$-R^3-$  is a divalent aromatic chain or aromatic chain which optionally includes one or more divalent heteroatoms or carbonyl groups in the chain; and

$Z^3$  is a moiety of the formula:

30  $-N(R^4)C(O)N(R^4)$ ,  $-C(R^4)_2-X-CR^4=C(R^4)_2$ ,  $-NH(R^4)_2$ ,



35

- 13 -

$N(R^4)_2$ ,  $-N=C=O$ ,  $-C(O)OR^4-C(O)OM^+$ , and the like;

p is an integer of from about 3 to about 201;

X is Cl, Br or I;

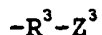
M is a metal cation such as  $Li^+$ ,  $Na^+$  and  $K^+$ ; and

5  $R^4$  is the same or different at each occurrence and is the hydrogen or alkyl (preferably alkyl having from 1 to about 10 carbon atoms, more preferably having from 1 to about 6 carbon atoms and most preferably from 1 to about 4 carbon atoms).

10 In the most preferred embodiments of the invention reactive silane agents are of the above formula in which:

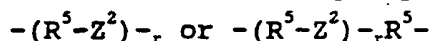
(-) is a covalent bond between the silicon atom and the surface of the platelet;

15 R is a moiety of the formula



wherein:

$-R^3-$  is divalent substituted or unsubstituted alkylphenylene, alkylphenylenealkylene or a  
20 divalent moiety selected from the group consisting of:



wherein:

$R^5$  is the same or different at each occurrence and is substituted or unsubstituted alkylene or phenylene  
25 (preferably where the aliphatic moieties include from 1 to about 10 carbon atoms, more preferably from 1 to about 7 carbon atoms and most preferably from 1 to about 4 carbon atoms) wherein permissible substituents are one or more hydroxy, cyano, or alkoxy or alkyl  
30 (preferably having from 1 to about 10 carbon atoms, more preferably having from 1 to about 7 carbon atoms and most preferably having from 1 to about 4 carbon atoms); and

- 14 -

r is an integer equal to or greater than 1  
(preferably from 1 to about 15, more preferably from 1  
to about 10 and most preferably from 2 to about 6);

-Z<sup>2</sup>- is the same or different at each occurrence  
5 and is -O-, -NH-, -C(O)-, -OC(O)-, -N(H)C(O)- or -  
N(H)C(O)N(H)-;

Z<sub>3</sub> is a moiety selected from the group consisting  
of -CH<sub>2</sub>X, -CH=CH<sub>2</sub>, -NH<sub>2</sub>, -OH, -O<sup>-</sup>M<sup>+</sup>,  $\text{HC}=\overset{\text{O}}{\text{C}}\text{H}_2$ , -C(O)X, -SH,  
10 -S<sup>-</sup>M<sup>+</sup>, -S<sub>2</sub>H, -S<sub>4</sub>H, -C(O)NH<sub>2</sub>, -NC(O)-[C(H)<sub>2</sub>]<sub>p</sub>, and  
-N=C=O;

X is Cl, Br or I;

M<sup>+</sup> is a metal cation such as Li<sup>+</sup>, Na<sup>+</sup> and K<sup>+</sup>; and

P is an integer from about 3 to about 20.


15 Silanes having reactive substituents are selected  
for particular classes of matrix polymers based on the  
reactivity and specifically of the reactive moiety.  
For example, polyamides are acid terminated and/or  
amine terminated, and polyesters are acid terminated  
20 and/or hydroxy terminated. Thereof, reactive  
functional groups which react with acid, amine or  
hydroxy functions to form covalent bonds can be  
conveniently used with polyesters and polyamides.  
Specific reactive functions such as -NH<sub>2</sub>, -N=C=O,  
25 CONH<sub>2</sub>, -OH, -O<sup>-</sup>M<sup>+</sup> (where M is a metal cation), -C(O)X  
(where X is Cl, Br, or I) and the like may be  
included in the reactive silane compound to react with  
reactive functionalities contained in polyesters and  
polyamide.

30 Similarly, silanes containing functions such as  
-NH<sub>2</sub>, -CH<sub>2</sub>-X (where X is Cl, Br or I), -CH<sub>2</sub>=CH<sub>2</sub>, -SH, S<sup>+</sup>M<sup>+</sup>  
(where M<sup>+</sup> is a metal cation such as Na<sup>+</sup>, Li<sup>+</sup> and K<sup>+</sup>) and  
S<sub>4</sub>H can be conveniently reacted with polyolefins and  
halogenated polyolefins such as poly(ethylene),  
35 poly(propylene), poly(chlorotrifluoroethylene) or



- 15 -

polyolefin elastomers such as butyl rubber to form covalent bonds between the polyolefins and the reactive silane. Likewise, polyvinyls such as poly(vinyl chloride), poly(co-ethylene vinyl alcohol) and the like  
5 can be reacted with silanes containing  
-NH<sub>2</sub>, -CH<sub>2</sub>-X (wherein X is Cl, Br and I), -OH,

-CH-CH<sub>2</sub>, -O<sup>-</sup>M<sup>+</sup> (where M is a metal cation such as Li<sup>+</sup>, Na<sup>+</sup> and K<sup>+</sup>), and the like.

10 More preferred silanes are those having substituents that react with thermoplastics and vulcanizable elastomers as described, for example, in the catalog of Huls America, Inc.. These include, silanes having alkoxy, acyloxy, amino, and halo  
15 functional groups which may be reacted with intercalated layered material in an organic solvent such as propanol, toluene, and dioxane. Most preferred reactive silanes are alkoxy and acyloxy substituted silanes which hydrolyze slowly in water and may be used  
20 to treat aqueous dispersions of unintercalated layered material. The reactive silanes of choice include isocyanatopropyltriethoxysilane and 1-trimethoxysilyl-2-(m,p-chloromethyl)phenylethane.

Layered material may be derivatized by a single  
25 silane, or by a mixture of silanes, or by a mixture of one or more silanes with one or more other swelling/compatibilizing agents such as one or more onium salts as for example such salts which have moieties which are compatible with the polymer forming  
30 the matrix. In the preferred embodiments of the invention the moieties are such that the swelling and compatibilizing agents are lipophobic such that the surface tension, at 20°C, of the derivatized particle is preferably less than or equal to about 55 dyne/cm.  
35 More preferably, between about 55 and 15 dyne/cm, and

- 16 -

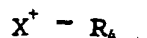
preferably between 45 and 20 dyne/cm, as determined by measuring the contact angles made by sessile drops of liquids on the solid surfaces. Such agents will preferably include a lipophilic portion as for example

5 a long chain alkyl, alkenyl or alkylaryl group (preferably of more than about 9 aliphatic carbon atoms). Such agents are well known in the art and include onium compounds having long chain alkyl groups such as octadecyl, dodecyl, decyl, octyl novyl, and the

10 like. Such optional onium salts are preferably the salts of primary and secondary ammonium radicals because of their heat stability. In this way the surface energy of the platelet particles and the number of polymer-reactive sites may be varied to optimize

15 platelet particle dispersion, polymer-particle compatibility, and polymer-particle bonding. Illustrative of useful onium species such as ammonium (primary, secondary, tertiary, and quaternary), phosphonium or sulfonium derivatives of aliphatic,

20 aromatic or arylaliphatic amines, phosphines and sulfides. Illustrative of such optional onium compounds are oxonium compounds of the formula:



where  $X^+$  is an ammonium, sulfonium or phosphonium

25 radical and  $R_n$  is an organic radical as for example substituted or unsubstituted alkyl, cycloalkenyl, cycloalkyl, aryl, or alkylaryl, either unsubstituted or substituted with amino, alkylamino, dialkylamino, nitro, azido, alkenyl, alkoxy, cycloalkyl,

30 cycloalkenyl, alkanoyl, alkylthio, alkyl, aryloxy, arylalkylamino, alkylamino, arylamino, dialkylamino, diarylamino, aryl, alkylsulfinyl, aryloxy, alkylsulfinyl, alkylsulfonyl, arylthio, arylsulfinyl,

- 17 -

alkoxycarbonyl, arylsulfonyl, alkylsilane, and a moiety of the formula:



5

wherein  $R_6$  is alkyl, cycloalkyl, or aryl,  $R_3$  is hydrogen, alkyl, or aryl, and  $Z$  is  $-O-$  or  $-NR_7-$ , where  $R_7$  is hydrogen, alkyl, aryl or silylalkyl.

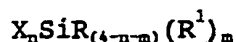
The amount of reactive silane swelling agent/compatibilizing agent intercalated into swellable layered materials useful in this invention may vary substantially provided that the amount is effective to swell and to compatibilize the layers of the intercalated layered material to the extent required to provide the desired substantially uniform dispersion. In the preferred embodiments of the invention, amounts of agents employed will be equal to or greater than about 1 m moles/100g of layered material. In the more referred embodiments of the invention the amount of the agent will range from about 2 mmole/100 g of layered material to about 200 mmole/100 g of layered material. Most preferred amounts are from about 20 mmole/100 g to about 120 mmole/100 g. In the case of the preferred smectite clay minerals, the most preferred amounts are from about 20 mmole/100 g to about 100 mmole/100 g of layered material.

Swellable and polymer-compatible intercalated layered material can be formed by any method. The reactive organo silane swelling/compatibilizing agents may be introduced into the interlayer spaces of the swellable layered material by any suitable method as, for example, by insertion of neutral molecules using conventional procedures. Insertion of neutral molecules may be performed by exposing finely divided layered material to intercalants in the form of a gas,

- 18 -

neat liquid, finely divided solid, or solute in a solvent which, preferably swells the layered material. Insertion is generally aided by exposure of the mixture of intercalant and layered material to heat, ultrasonic  
 5 cavitation, or microwaves of a montmorillonite or a saponite in water, may be heated to about 80°C and stirred using a high speed homogenizer mixer, in a concentration low enough to yield a low viscosity dispersion from which non-dispersible particles can be  
 10 separated by sedimentation (mineral concentration of about 2% by weight, or 5% to 15% with addition of a peptizing agent such as sodium hexametaphosphate). The dispersion is combined with a solution of an onium material such as an ammonium salt (as, for example the  
 15 hydrochlorides of octadecylamine, 11-aminoundecanoic acid, dioctylamine, dimethyldodecylamine, methyloctadecylamine, dimethyldidodecylamine, and the like) such that the mole ratio of ammonium salt to exchangeable ions in the mineral is between 0.5 and 5.  
 20 Intercalated layered materials are formed which are intercalated partially or wholly can be prepared by treatment of a suitable layered material with reactive organo silane swelling/compatibilizing agents of the formula:

25



where R and R<sup>1</sup> are as described above and X is a leaving group which is displaceable by or reactive with  
 30 oxide functions on the surface of said layers such as halo, alkoxy, acyloxy, amine and the like such as N-(2-aminoethyl-3-aminopropyl trimethoxysilane, -3-isocyanatopropyltriethoxysilane, diethylphosphatoethyltriethoxysilane,  
 35 trimethoxysilylpropylisothiuronium-chloride,

- 19 -

N-(3-trimethoxysilylpropyl)-N-methyl-N,N-diallylammonium-chloride N-(3-acyloxy-2-hydroxypropyl)-3-aminopropyl triethoxysilane, N-(triethoxysilylpropyl)urea, 3-amino propylmethyl diethoxysilane, 1-trimethoxysilyl-2-(p,m-chloromethyl)-phenylethane, (aminoethylaminomethyl)phenylethyltrimethoxysilane, trimethoxysilylpropyldiethylenetri amine, vinyltriethoxysilane, vinyltris(t-butylperoxy)silane, 3-(n-styrylmethyl-2-aminoethylamino)propyltrimethoxysilane hydrochloride, phenyltriethoxysilane, 3-mercaptopropylmethyldimethoxysilane, 3-glycidoxypropyltrimethoxysilane, bis(2-hydroxyethyl)-aminopropyltriethoxysilane, (3-glycidoxypropyl)methyldiethoxysilane, bis-[3-(triethoxysilyl)propyl]tetrasulfide, N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane, 3-aminopropyltriethoxysilane, allyltrimethoxysilane, vinyltris(methylethylketoximine)silane, and the like. Such intercalated layered materials may be prepared by any convenient method. For example, an alkoxy or acyloxy silanes, dissolved in water or a mixture of water and a polar organic solvent such as methanol, ethanol, propanol, acetone, methyl ethyl ketone and the like, may be combined with a dispersion of layered material in a like solution at about 50°C to about 90°C. The reactive silane intercalated layered material resulting from this combination may be collected by filtration dried and ground into powder. Other silanes (reactive or non-reactive) and onium cation may be combined in the same solution, or may be added in separate steps to the dispersion of layered material. Alternatively, layered material may be intercalated wholly or in party by reactive silane

- 20 -

swelling/compatibilizing agent by treating a swellable layered material already intercalated with an onium cation with the reactive silane. The reactive organosilane compound is preferably in a swelling liquid, such as dioxane, glyme, diglyme, dimethylsulfoxide, methylethylketone, and the like, or by treating an aqueous suspension of a layered material with water-soluble reactive organo silane swelling/compatibilizing agents such as trialcoxysilanes. In the preferred embodiments, silane intercalated swellable, polymer compatible intercalated layered material is formed as follows. Onium-intercalated layered materials are suspended and swollen in a swelling organic liquid, such as toluene, propanol, dioxane, glyme, diglyme, dimethylsulfoxide, methylethylketone, and the like, and treated with a trialcoxysilane. For example, montmorillonite intercalated with octadecylammonium cation, at about 80 mmole of ammonium cation/100 g mineral, is combined with dioxane to form a 5% by weight suspension which is heated to 60°C and combined with a dioxane solution of aminoethylaminopropyl trimethoxysilane, such that the ratio of silane to mineral is about 20 mmole/100 g. The silane displaces all or a portion of the ammonium cation. The layers totally or partially intercalated with the reactive silane swelling/compatibilizing agent may be separated from the solution by some suitable method such as filtration or centrifugation, followed by rinsing in fresh water, rough drying, and ball milling to about 100 mesh powder. The powder may be rigorously dried at 100°C to 160°C in vacuum for 8 to 24 h in the presence of a drying agent such as phosphorous pentoxide, to provide the desired swellable/polymer compatible intercalated layered material.

- 21 -

The onium ion intercalated precursor may be formed by ion exchange by ionic molecules may be performed by suspending the layered material in a relatively volatile liquid which is capable of both exfoliating and dispersing the layers of the intercalated layered material and dissolving a salt of the ionic intercalant as well as the resulting salt of the ion displaced from the layered material (e.g.,  $\text{Na}^+$ ,  $\text{Mg}^{+2}$ ,  $\text{Ca}^{+2}$ ), adding the salt of the ionic intercalant, and removing the layered material (now complexed with the new intercalant) from the liquid (now containing the dissolved salt of the displaced ion). For example, swellable layered minerals such as montmorillonite and hectorite (having primarily  $\text{Na}^+$  cations in the interlayer spaces) intercalate water to the point that the layers are exfoliated and dispersed uniformly in water. Dispersion in water is generally aided by mixing with relatively high shear. An onium material such as the hydrochloride salt of dimethyldodecylamine is then added in the desired amount after which the layers complexed with the ammonium cation are separated from the dispersion, washed of residual  $\text{NaCl}$ , and dried.

The amount of intercalated layered material included in the mixture may vary widely but generally at least about 0.001% by weight of the composite preferably from about 0.001 to about 60% by weight of the composite, more preferably from about 0.01 to about 20% by weight of the composite and most preferably from about 0.1 to about 10% by weight of the composite. The amount of material employed in any particular situation will depend to a significant extent on the intended use. For example, relatively, larger amounts of platelet particles (exclusive of intercalant since the intercalant content in the layered material may vary), i.e. from about 15% to about 30% by wgt. of the

- 22 -

mixture, are used in applications where articles are formed by stamping. Substantially enhanced barrier properties and heat resistance (deflection temperature under load, DTUL) are imparted by platelet particle concentrations greater than about 2.5%. Similarly, substantially enhanced strength is imparted by platelet particle concentrations greater than about 1.5%. When it is desired to preserve such properties as toughness (impact resistance) and elongation which are generally adversely affected by high loadings of any filler material including the nano-scale layered materials of this invention, it is preferred that the silicate loading be less than about 0.5%. Particle concentration within the range 0.05 to 0.5% significantly enhance modulus, dimensional stability, and wet strength (the latter in the case of polyamides). Concentrations below 0.5% can be employed to increase melt viscosity (useful in film extrusion and in fiber melt spinning) or they may be employed in selected polymers to stabilize a particular crystalline phase (useful in the case of nylon 6 to stabilize the gamma phase) or limit spherulite size which reduces haze and increases optical clarity. In general, the amount of material employed is less than about 60% by weight of the mixture. The amount of material employed is preferably from about 0.01% to about 20 % by weight of the mixture, more preferably from about 0.05% to about 10% by weight of the mixture, and most preferably from about 0.05% to about 8% by weight.

30       The second essential ingredient of the flowable mixture is a melt processible polymer. Polymers for use in the process of this invention may vary widely, the only requirement is that they are melt processible. As used herein, a "polymer" in a substance composed of

35       ten or more recurring monomeric units which may be the



- 23 -

same or different. In the preferred embodiments of the invention, the polymer includes at least ten recurring monomeric units. The upper limit to the number of recurring monomeric units is not critical, provided  
5 that the melt index of the polymer under use conditions is such that the polymer forms a flowable mixture. The polymer more preferably includes at least about 20 recurring monomeric units and most preferably includes at least about 30 recurring monomeric units. In the  
10 embodiments of this invention of choice, the number of recurring units is such that the polymer has a melt index of from about 0.01 to about 12 grams per 10 minutes at the processing temperature.

Useful polymers are thermoplastic polymers or  
15 mixtures thereof, and vulcanizable and thermoplastic rubbers. Thermoplastic resins for use in the practice of this invention may vary widely. Illustrative of useful thermoplastic resins are polylactones such as poly(pivalolactone), poly(caprolactone) and the like;  
20 polyurethanes derived from reaction of diisocyanates such as 1,5-naphthalene diisocyanate, 3,3'-dimethyl-4,4'diphenyl-methane diisocyanate, 4,4'-diphenylisopropylidene diisocyanate, 4,4'-diisocyanatodiphenylmethane and the like and linear  
25 long-chain diols such as poly(tetramethylene adipate), poly(ethylene succinate), polyether diols and the like; polycarbonates such as poly[methane bis(4-phenyl) carbonate], poly[1,1-ether bis(4-phenyl) carbonate], and the like; polysulfones; polyether ether ketones;  
30 polyamides such as poly (4-amino butyric acid), poly(hexamethylene adipamide), poly(6-aminohexanoic acid), poly(2,2,2-trimethyl hexamethylene terephthalamide), and the like; polyesters such as  
35 dimethylene terephthalate), poly(ethylene oxybenzoate)

- 24 -

- (A-Tell), poly(para-hydroxy benzoate) (Ekonol), polyethylene terephthalate, polybutylene terephthalate and the like; poly(arylene oxides) such as poly(2,6-dimethyl-1,4-phenylene oxide), and the like;
- 5 poly(arylene sulfides) such as poly(phenylene sulfide) and the like; polyetherimides; vinyl polymers and their copolymers such as polyvinyl alcohol, polyvinyl chloride, and the like; polyacrylics, polyacrylate and their copolymers such as polyethyl acrylate,
- 10 polymethylmethacrylate, polyacrylonitrile, methyl methacrylate-styrene copolymers, ethylene-ethyl acrylate copolymers, methacrylated butadiene-styrene copolymers and the like; polyolefins such as poly(propylene), poly(ethylene), poly(styrene), and the
- 15 like; ionomers; poly(epichlorohydrins); poly(urethane) such as the polymerization product of diols such as glycerin, pentaerythritol, polyether polyols, polyester polyols and the like with a polyisocyanate such as 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 4,4'-
- 20 diphenylmethane diisocyanate, and the like; and polysulfones such as the reaction product of the sodium salt of 2,2-bis(4-hydroxyphenyl) propane and 4,4'-dichlorodiphenyl sulfone; furan resins such as poly(furan); cellulose ester plastics such as cellulose
- 25 acetate, cellulose acetate butyrate, and the like; silicones such as poly(dimethyl siloxane), poly(dimethyl siloxane co-phenylmethyl siloxane), and the like; protein plastics; and blends of two or more of the foregoing.
- 30 Vulcanizable and thermoplastic rubbers useful in the practice of this invention may also vary widely. Illustrative of such rubbers are brominated butyl rubber, chlorinated butyl rubber, polyurethane elastomers, fluoroelastomers, polyester elastomers,
- 35 butadiene/acrylonitrile elastomers, silicone

- 25 -

elastomers, poly(butadiene), poly(isobutylene), ethylene-propylene copolymers, ethylene-propylene-diene terpolymers, sulfonated ethylene-propylene-diene terpolymers, poly(chloroprene), poly(2,3-  
5 dimethylbutadiene), poly(butadiene-pentadiene), chlorosulphonated poly(ethylenes), poly(sulfide) elastomers, block copolymers, made up of segments of glassy or crystalline blocks such as poly(styrene), poly(vinyl-toluene), poly(t-butyl styrene), polyester  
10 and the like and the elastomeric blocks such as poly(butadiene), poly(isoprene), ethylene-propylene copolymers, ethylene-butylene copolymers, polyether ester and the like as for example the copolymers in poly(styrene)-poly(butadiene)-poly(styrene) block  
15 copolymer manufactured by Shell Chemical Company under the trade name of Kraton®

More preferred polymers are thermoplastic polymers such as polyamides, polyesters, and polymers of alpha-beta unsaturated monomers and copolymers.

20 Most preferred polyamers for use in the practice of this invention are poly(caprolactam), poly(hexamethylene adipamide), poly(ethylene terephthalate), poly(butylene terephthalate), poly(1,4-cyclohexane dimethylene terephthalate),  
25 poly(ethylene) and ethylene copolymers. More preferred are poly(ethylene) and poly(propylene).

The mixture may include various optional components which are additives commonly employed with polymers. Such optional components include nucleating agents,  
30 fillers, plasticizers, impact modifiers, chain extenders, plasticizers, colorants, mold release lubricants, antistatic agents, pigments, fire retardants, and the like. These optional components and appropriate amounts are well known to those of

- 26 -

skill in the art, accordingly, only the preferred optional components will be described herein in detail.

In the second step of the process of this invention, the flowable mixture is subjected to a shear  
5 having an "effective shear rate". As used herein, an "effective shear rate" is a shear rate [as shear rate is defined in Ferdinand Rodriguez, "Principles of Polymers Systems", McGraw-Hill Book Company, New York (1982)] which is effective to delaminate at least about  
10 90% by weight of the intercalated material to form platelet particles described above, and provide a composition comprising a polymeric matrix having platelet particles substantially homogeneously dispersed therein. In the preferred embodiments of the  
15 invention, the shear rate is greater than about  $10 \text{ sec}^{-1}$ . In these preferred embodiments of the invention, the upper limit for the shear rate is not critical provided that the shear rate is not so high as to physically degrade the polymer. In the particularly  
20 preferred embodiments of the invention, the shear rate is from greater than about  $10 \text{ sec}^{-1}$  to about  $20,000 \text{ sec}^{-1}$ , and in the most preferred embodiments of the invention the shear rate is from about  $100 \text{ sec}^{-1}$  to about  $10,000 \text{ sec}^{-1}$ .

25 Any method which can be used to apply a shear to a flowable mixture or any polymer melt can be used. The shearing action can be provided by any appropriate method, as for example by mechanical means, by thermal shock, by pressure alteration, or by ultrasonics.  
30 Methods useful in shearing melts are known in the art, and will not be described in great detail. In particularly useful procedures, the flowable polymer mixture is sheared by mechanical methods in which portions of the melt are caused to flow past other  
35 portions of the mixture by use of mechanical means such

- 27 -

as stirrers, Banbury® type mixers, Brabender® type mixers, long continuous mixers, and extrudes. Another procedure employs thermal shock in which shearing is achieved by alternatively raising or lowering the

5 temperature of the mixture causing thermal expansions and resulting in internal stresses which cause the shear. In still other procedures, shear is achieved by sudden pressure changes in pressure alteration methods; by ultrasonic techniques in which cavitation or

10 resonant vibrations which cause portions of the mixture to vibrate or to be excited at different phases and thus subjected to shear. These methods of shearing flowable polymer mixtures and polymer melts are merely representative of useful methods, and any method known

15 in the art for shearing flowable polymer mixtures and polymer melts may be used.

In the preferred embodiments of the invention, mechanical shearing methods are employed such as by extrusion, injection molding machines, Banbury® type

20 mixers, Brabender® type mixers and the like. In the more preferred embodiments of the invention, shearing is achieved by introducing the polymer melt at one end of the extruder (single or double screw) and receiving the sheared polymer at the other end of the extruder.

25 The temperature of the polymer melt, the length of the extruder, residence time of the melt in the extruder and the design of the extruder (single screw, twin screw, number of flights per unit length, channel depth, flight clearance, mixing zone etc.) are several

30 variables which control the amount of shear to be applied.

The process of this invention is preferably carried out in the absence of air, as for example in the presence of an inert gas, such as, argon, neon,

35 nitrogen or the like. The process can be carried out

- 28 -

in a batchwise or discontinuous fashion, as for example, carrying out the process in a sealed container. Alternatively, the process can be carried out in a continuous fashion in a single processing zone, as for example by use of an extruder, from which air is largely excluded, or in a plurality of such reaction zones in series or parallel.

Upon subjecting a flowable mixture of said swellable intercalated layered material and said polymer melt to shear mixing, at least about 80% by weight, preferably at least about 85% by weight, more preferably at least about 90% by weight and most preferably at least about 95% by weight of the layers of the material delaminate to form platelet particles substantially homogeneously dispersed in the polymer matrix. As used herein, "platelet particles" are particles having two relatively flat opposite faces wherein the thickness of which is the distance between the faces, which is relatively small compared to the size of the faces. As formed by this process, the platelet particles dispersed in matrix polymers have the thickness of the individual layers, or small multiples less than about 10, preferably less than about 5 and more preferably less than about 3 of the layers, and still more preferably 1 or 2 layers. In the preferred embodiments of this invention, intercalation of every interlayer space is complete so that all or substantially all individual layers delaminate one from the other to form separate platelet particles. In cases where intercalation is incomplete between some layers, those layers will not delaminate in the polymer melt, and will form platelet particles comprising those layers in a coplanar aggregate. These latter platelet particles still constitute nanoscale and nanodispersed fillers and provide enhanced

- 29 -

properties over and above those provided by conventional micro-scale fillers, as long as they are less than about 10 layers thick and preferably less than 5 layers thick. The other dimensions of the

5 platelet particles may vary greatly, but in the case of particles derived from clay minerals, the particle faces are roughly hexagonal or rectangular having average diameters between about 10,000 Å and about 50 Å with a maximum diameter and about 20,000 Å, such that

10 the aspect ratio length/thickness ranges from about 2000 to about 10 and an average thickness of less than about 50 Å with a maximum thickness of 100 Å. For the purposes of the present invention, the average diameter is defined as the diameter of a circle having an area

15 equal to the surface area of one broad surface face of the platelet shaped particle. In the preferred embodiments of the invention the average thickness of the platelet particles is equal to or less than about 20 Å with a maximum diameter of about 10,000 Å and the

20 average diameter is between 5,000 Å and 100 Å. Most preferably the average thickness is about from 5 to about 15 Å and the average diameter is from about 2,500 to about 150 Å with a maximum diameter of about 5,000 Å. The most preferred average diameter depends on both

25 the desired property of the nanocomposite and the ease of complete intercalation and delamination to form the nanocomposite structure. High aspect ratios, and therefore large average diameters, are generally preferred for reinforcement and barrier properties,

30 while layered materials having smaller platelets are preferred for their ease of delamination. Thus, for purposes of the nanocomposite properties, the most preferred average diameter is greater than about 150 Å, and, for purposes of delamination, it is less than

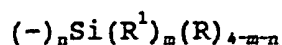
35 about 3000 Å with a maximum diameter of about 5,000 Å.

- 30 -

The average interparticle spacing between delaminated layers may vary widely after shearings, depending on the concentration of layered material. In general the higher the concentration of layered material in the polymer matrix particle the smaller the interparticle spacing; and conversely, the lower the concentration of layered material, the larger the interparticle spacing. In general, interparticle spacing is equal to or greater than 15Å. The interparticle spacing is preferably equal to or greater than about 20Å, more preferably equal to or greater than about 30Å and most preferably equal to or greater than about 50Å.

As used herein "uniformly dispersed" is defined as a degree of dispersion of the platelet shaped particles having a standard deviation in platelet particle density, down to a sampling volume of  $10^{-15} \text{ m}^3$ , which is preferably less than about 50% of the mean, more preferably less than about 30% of the mean, and most preferably less than about 20% of the mean as determined from estimates based on transmission electron microscopy.

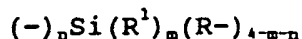
On delamination of the layers in the meet the reactive moiety of the organosilane swelling/compatibilizing agents covalently bonded to the surface of the platelets react with a polymer component of the polymeric matrix forming covalent bonds. Thus, the matrix is bonded to the surface of the particles by way of the residue of this invention. For example, where the silane bonded to the surface of the platelet is of the formula:





- 31 -

where  $n$ ,  $R^1$ ,  $m$  and  $R$  are as described below, during melt processing the agent reacts with a polymeric component to form a covalent bond such that the component and the surface of the platelet by a divalent residue of the  
 5 formula:



wherein  $R^-$  is a residue resulting from the reactive of  
 10 one or more of  $R$  groups with a polymer component of the polymer matrix.

The nanocomposites of this invention exhibit useful properties. For example, the nanocomposites of this invention exhibit enhance yield strength and tensile  
 15 modulus, even when exposed to polar media such as water or methanol, enhanced heat resistance and enhanced impact strength as compared to the compositions which does not include the dispersion layered material as compared to polymer composites which do not include  
 20 dispersed layered material and those composites which do include such composites which have been intercalated with reactive onium compounds as for example those described in U.S. Patent Nos. 4,739,007 and 4,810,734. The improvements in properties are obtained even though  
 25 smaller amounts of the layered material are employed. Various useful performance indices can be devised in order to jointly assess different performance aspects using a single number. Depending upon the nature of the devised index, comparisons can be made either  
 30 between samples containing the same loading of layered material or the index can be more broadly applied to polymers having different loadings of clay. For example, the effect of adding nanoscale particulate fillers dispersed platelet particles to a polymer  
 35 typically increases tensile modulus, ultimate tensile

- 32 -

strength and heat deflection temperature while decreasing ultimate elongation and impact strength. In the case where combinations of high modulus ( $Y$ ) and high ultimate elongation ( $\Delta L/L$ ) are required, a useful performance index for comparing samples with similar particulate loading is  $Y(\Delta L/L)$ . Likewise, when tensile strength( $S$ ) combined with high ultimate elongation is sought, a useful performance index for comparing samples with similar loading levels is  $S(\Delta L/L)$ . The preferred embodiments of the present invention provide a  $Y(\Delta L/L)$  of above about 660 MPa (preferably equal to or greater than about 800 MPa more preferably equal to or greater than about 1000 MPa and most preferably equal to or greater than about 1200 MPa) for a loading of about 2% of nanodispersed layered material such as montmorillonite in a melt processible polymer such as nylon 6. In contrast, the prior art patents on in-reactor nanocomposite blends (U.S. 4,739,007 and U.S. 4,810,734) provide a maximum  $Y(\Delta L/L)$  of about 660 MPa. Also, preferred embodiments of the present invention provide a  $S(\Delta L/L)$  of above about 20 MPa (preferably equal to or greater than about 25 MPa and more preferably equal to or greater than about 30 MPa) for a loading of about 2% intercalated layered material such as montmorillonite, while the maximum value for this figure of merit obtained in the above mentioned in-reactor process patents is about 20 MPa at 2% loading. While we do not wish to be bound by any theory, it is believed that the unique properties of the nanocomposites of this invention result from the use of reactive organosilane swelling/compatibilizing agents which are compatible with and which react with the matrix polymer to become part of the main chain of the matrix polymer and which react with the surface of the layered material to form covalent bonds. The preferred

- 33 -

reactive organosilane swelling/compatibilizing agents of this invention, which remain bonded to the particle surface, interact with the matrix polymer by covalent bond formation with the matrix polymer.

- 5 Nanocomposites having particularly attractive combinations of modulus, tensile strength and ultimate elongation are formed using swelling/compatibilizing agents, which are bonded to the particle surface and to the matrix polymer and which include polymer-
- 10 interacting moiety projects away from the particle surface which is compatible with the matrix polymer. This function is best performed by silane compounds and onium compounds (especially ammonium compounds) of the type having a lipophilic moiety such that the surface
- 15 tension, at 20°C, of the derivatized particle is between about 55 and 15 dyne/cm, and preferably between 45 and 20 dyne/cm, as determined by measuring the contact angles made by sessile drops of liquids on the solid surfaces. Illustrative of these preferred silane
- 20 compounds are silanes of the formula;  $-\text{SiR}_1\text{R}_2\text{R}_3$  where  $\text{R}_1$  and  $\text{R}_2$  are the same or different at each occurrence and are alkyl, alkoxy or oxysilane; and  $\text{R}_3$  is organic groups which is compatible and reactive with the polymer such as aminolalkyl, chloromethylaromatic,
- 25 isocyanato alkyl, caprolactam-block isocyanato-alkyl and the like. Preferably, the silane compound on the particle has a surface tension at 20°C of less than about 55 dyne/cm. The nanocomposite compositions according to the invention are thermoplastic and, in
- 30 some cases, vulcanizable materials from which molded articles of manufacture having valuable properties can be produced by conventional shaping processes, such as melt spinning, casting, vacuum molding, sheet molding, injection molding and extruding. Examples of such
- 35 molded articles are components for technical equipment,

- 34 -

apparatus castings, household equipment, sports equipment, bottles, containers, components for the electrical and electronics industries, car components, circuits, fibers, semi-finished products which can be

5 shaped by machining and the like. The use of the materials for coating articles by means of powder coating processes is also possible, as is their use as hot-melt adhesives. The molding compositions according to the invention are outstandingly suitable for

10 specific applications of all types since their spectrum of properties can be modified in the desired direction in manifold ways. Such molded products of this invention will derive one or more advantages over products molded with polymers having no nanodispersed

15 platelet particles including increased modulus, stiffness, wet strength, dimensional stability, and heat deflection temperature, and decreased moisture absorption, flammability, permeability, and molding cycle time.

20 The molding compositions according to the invention are outstandingly suitable for the production of sheets and panels having valuable properties. Such sheets and panels may be shaped by conventional processes such as vacuum processing or by hot pressing to form useful

25 objects. The sheets and panels according to the invention are also suitable as coating materials for other materials comprising, for example, wood, glass, ceramic, metal or other plastics, and outstanding strengths can be achieved using conventional adhesion

30 promoters, for example, those based on vinyl resins. The sheets and panels can also be laminated with other plastic films and this is preferably effected by co-extrusion, the sheets being bonded in the molten state. The surfaces of the sheets and panels, including those

35 in the embossed form, can be improved or finished by

- 35 -

conventional methods, for example by lacquering or by the application of protective films.

The compositions of this invention are especially useful for fabrication of extruded films and film  
5 laminates, as for example, films for use in food packaging. Such films can be fabricated using conventional film extrusion techniques. The films are preferably from about 10 to about 100 microns, more preferably from about 20 to about 100 microns and most  
10 preferably from about 25 to about 75 microns in thickness. In the film, the major plane of the platelet fillers is substantially parallel to the major plane of the film. The extent of parallelism of particles and film can be determined by X-ray analysis.  
15 X-ray analysis is a useful way to described the crystallinity and orientation of polymer crystals and the orientation of platelet particles. A convenient method of X-ray analysis is that described in Hernans, P.H. and Weidinger A., Makromol Chemie, Vol. 44, pp.  
20 24-36 (1961), hereby incorporated by reference.

For the purpose of the present invention Op, the platelet orientation factor, is an indication of the platelet particle orientation in the film. The Op was determined by making azimuthal scans from densitometer  
25 tracings of the X-ray photographs which were obtained by exposing the edge of the film to the incident X-rays. The angle is the angle between the reference direction, the normal to the film, and the normal to the plane of interest, the major plane of the platelet.  
30 The Op values were calculated as the average cosine square ( $\langle \cos^2 \rangle$ ) for the normal to the flat faces of the platelet particles. An Op of 1.0 indicates that the faces of the platelets are completely parallel to the plane of the film. An Op of 0.0 indicates that the  
35 faces of the platelets are perpendicular to the plane

- 36 -

of the film. The Op of the platelets in the film of the present invention is preferably from about 0.70 to about 1.0, more preferably from about 0.90 to about 1.0 and most preferably from about 0.95 to about 1.0. Such  
5 preferred orientation of platelet particles results in enhanced barrier properties and increased tare strength.

The homogeneously distributed platelet particles and polymer are formed into a film by suitable film-  
10 forming methods. Typically, the composition is melted and forced through a film forming die. The die can be a flat die or a circular die. A typical flat die is a hanger shaped die, and a typical circular die is a tubular film die.

15 The film of the nanocomposite of the present invention may go through steps to cause the platelets to be further oriented so the major planes through the platelets are substantially parallel to the major plane through the film. A method to do this is to biaxially  
20 stretch the film. For example, the film is stretched in the axial or machine direction by tension rollers pulling the film as it is extruded from the die. The film is simultaneously stretched in the transverse direction by clamping the edges of the film and drawing  
25 them apart. Alternatively, the film is stretched in the transverse direction by using a tubular film die and blowing the film up as it passes from the tubular film die. The films of this invention may exhibit one or more of the following benefits: increased modulus,  
30 wet strength, and dimensional stability, and decreased moisture adsorption and permeability to gases such as oxygen and liquids such as water, alcohols and other solvents.

- 37 -

The following specific examples are presented to more particularly illustrate the invention and are not to be construed as limitations thereon.

5

EXAMPLE 1

Two different nylon 6 nanocomposites of montmorillonites partially derivatized with polyamide-reactive silanes were prepared by extruding nylon 6 pellets along with powdered derivatized  
10 montmorillonite. The silane-derivatized montmorillonites were prepared by adding alkoxysilane to a dispersion of montmorillonite-quaternary ammonium cation complex (Claytone AF™) in refluxing propanol (100g Claytone AF per 1000 mL propanol). The silanes  
15 used were (1) the reaction product of isocyanatopropyltriethoxysilane with caprolactam, referred to here as clay-caprolactamsilane, and (2) 1-trimethoxysilyl-2-(m,p-chloromethyl)phenylethane, referred to herein as clay-chloromethylphenyl silane.  
20 After 3 days at reflux each mixture was filtered, and the recovered derivatized clay was washed 4 times in fresh hot propanol and vacuum dried at 85°C. The compounding was performed using a Leistritz twinscrew extruder with a general purpose screw, and the  
25 extrudate was dried and injection molded. Injection molded samples of the nylon 6 nanocomposites and nylon 6 were tested for their tensile properties according to the procedures of ASTM D638 under the following conditions: dry as molded, after 14 day immersion in  
30 water at 20°C, and after 14 day immersion in methanol at 20°C. Dry as molded samples of the nylon 6 nanocomposites and nylon 6 were also tested for their notched impact strength according to the procedures of ASTM D256, and for their heat deflection temperature  
35 under a 264 psi load (DTUL 264 psi) according to the

- 38 -

procedures of ASTM D648. The results are set forth in  
Tables 1, 2, and 3.



**Table 1. Mechanical Properties Dry as Molded**

Exp. No.	Composition	tensile modulus, psi (MPa)	yield strength, psi (MPa)	ultimate elongation %	notched impact ft-lb	DTUL 264 psi, (C)
1	1.9% clay-caprolactamsilane	573,000 (3960)	12,800 (88)	12	0.9	76
2	1.1% clay-chloromethyl phenylsilane	544,000 (3760)	12,600 (87)	12	0.9	72
3	nylon 6 <sup>a</sup>	400,000 (2760)	11,000 (76)	80	0.9	56

**Table 2. Tensile Properties, After 14 Days Water at 20°C**

Exp. No.	Composition	tensile modulus, psi (MPa)	yield strength, psi (MPa)	ultimate elongation %
1	nylon 6 and 1.9% clay-caprolactamsilane	223,000 (1540)	6,600 (46)	150
2	nylon 6 and 1.1% clay-chloromethyl phenylsilane	226,000 (1560)	6,500 (45)	140
3	nylon 6	117,000 (810)	4,300 (30)	250

**Table 3. Tensile Properties, After 14 Days in Methanol at 20°C**

Exp. No.	Composition	tensile modulus, psi (MPa)	yield strength, psi (MPa)	ultimate elongation %
1	1.9% clay-caprolactamsilane	103,000 (710)	4,300 (30)	> 200
2	1.1% clay-chloromethyl phenylsilane	105,000 (725)	4,200 (29)	> 200
3	nylon 6 <sup>a</sup>	72,000 (500)	3,400 (23)	> 200

- 40 -

## COMPARATIVE EXAMPLE 2

A series of experiments were carried out to show the enhanced properties of the composite of this invention which flow from the use of the reactive silane swelling/compatibilizing agent in comparison with the same properties of composites in which the swelling and compatibilizing agent is a reactive onium compound of the type described in U.S.S Patent No. 4,739,007. Two nylon 6 nanocomposites of montmorillonite derivatized with ammonium cations were prepared by extruding nylon 6 pellets along with powdered derivatized montmorillonite. The montmorillonite complex of protonated 11-aminoundecanoic acid cation was prepared by adding an aqueous solution of the aminoacid HCl salt to an aqueous dispersion of montmorillonite (about 5% montmorillonite) at 80°C and under high shear stirring. The montmorillonite complex of protonated octadecylamine cation was prepared by adding water/methanol (1:1) solution of the amine HCl salt to a dispersion of montmorillonite (about 5% montmorillonite) in a liquid of the same composition at 80°C and under high shear stirring. The ammonium-derivatized montmorillonite was compounded, molded, and tested according to the procedure of Example 1. The results are set forth in Tables 4, 5, and 6 in side by side comparison with the results of the testing of the composite of this invention.

- 41 -

**Table 4. Mechanical Properties Dry as Molded**

Ex. No.	Composition	tensile modulus, psi (MPa)	yield strength, psi (MPa)	ultimate elongation %	notched impact ft-lb	DTUL 264 psi, (C)
1	1.9% clay-caprolactams ilane	573,000 (3960)	12,800 (88)	12	0.9	76
2	1.1% clay-cloromethyl phenylsilane	544,000 (3760)	12,600 (87)	12	0.9	72
3	1.8 % clay-aminoundecanoic acid	480,000 (3320)	13,300 (29)	5	0.4	70
4	nylon 6 <sup>a</sup>	400,000 (2760)	11,000 (76)	80	0.9	56

10

**Table 5. Tensile Properties, After 14 Days Water at 20°C**

Exp. No.	Composition	tensile modulus, psi (MPa)	yield strength, psi (MPa)	ultimate elongation %
1	nylon 6 and 1.9% clay-caprolactams ilane	223,000 (1540)	6,600 (46)	150
2	nylon 6 and 1.1 % clay-cloromethyl phenylsilane	226,000 (1560)	6,500 (45)	140
3	1.8 % clay-aminoundecanoic acid	190,00 (1310)	6,000 (41)	60
4	nylon 6	117,000 (810)	4,300 (30)	250

15

- 42 -

Table 6. Tensile Properties, After 14 Days in Methanol at 20°C

Exp. No.	Composition	tensile modulus, psi (MPa)	yield strength, psi (MPa)	ultimate elongation %
1	1.9% clay- caprolactams ilane	103,000 ( 710)	4,300 (30)	>200
2	1.1% clay- chloromethyl phenylsilane	105,000 ( 725)	4,200 (29)	>200
3	1.8% clay- aminoundec anoic acid	100,000 (690)	3,900 (27)	>200
4	nylon 6°	72,000 ( 500)	3,400 (23)	>200

As shown in Table 5, the two reactive silanes

10 imparted dry impact strength and tensile strength in the presence of water and methanol that was superior to that exhibited by comparable nanocomposites having the identical montmorillonite derivatized with a reactive ammonium cation (protonated 11-aminoundecanoic acid).

15 The reactive silanes also imparted a combination of tensile modulus and ultimate elongation, both dry and in the presence of water, that was superior to the clay-aminoundecanoic acid nanocomposites. The reactive silanes also imparted DTUL 264 psi values that were

20 higher than those exhibited by clay-aminoundecanoic acid nanocomposites.

- 43 -

WHAT IS CLAIMED IS:

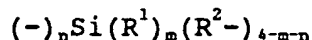
1. Composite material comprising a polymer matrix comprising a melt processible polymer and dispersed platelet particles having average thicknesses of less than 50 Å and a maximum thickness of less than about 100Å, and having an organo silane residue species covalently to surfaces of said particles and organo silane species covalently bonded to a polymer species in the polymer matrix, said platelet particles being present in an amount less than about 60% by weight of the composite material.

2. Composite material of claim 1 wherein said platelet particles are derived from phyllosilicates.

3. Composite material of claim 2 wherein said 5. Composite material of claim 5 wherein said phyllosilicates are smectite clay materials.

4. Composite material of claim 3 wherein said smectite clay materials are montmorillonite or hectorite.

5. Composite material of claim 3 wherein said organo residue species is of the formula:



wherein:

(-) is a covalent bond between the silicon atom and the surface of the platelet;

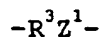
$\text{R}^1$  is an organic radical;

$-\text{R}^2-$  is a divalent organic chain which bonds the silicon atom to a polymer component of the polymer matrix;

$m$  is 0, 1 or 2; and

6. Composite material of claim 5 wherein:

$-\text{R}^2-$  is an aromatic or aliphatic moiety of the formula:



- 44 -

wherein:

-R<sup>3</sup>- is a divalent aromatic chain or divalent aliphatic chain or a divalent aromatic or an aliphatic group having one or more divalent heteroatoms or  
 5 carbonyl groups in the chain; and

-Z<sup>1</sup>- is the moiety which is directly bonded to the polymeric component and is selected from the group consisting of --N(R<sup>4</sup>)C(O)N(R<sup>4</sup>)-, -[C(R<sup>4</sup>)<sub>2</sub>]-, -O-, -NR<sup>4</sup>-, -C(O)-, -S-, -S(O<sub>2</sub>)-, -S<sub>4</sub>-, -S<sub>2</sub>-, -S(O)-, -S(O<sub>2</sub>)-, -OC(O)-, -  
 10 C(O)N(R<sup>4</sup>)- or -N(R<sup>4</sup>)C(O)-;

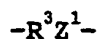
R<sup>4</sup> is the same or different at each occurrence hydrogen or alkyl having from 1 to about 4 carbon atoms; and

R<sub>1</sub> is alkyl, cycloalkyl, alkoxyalkyl, phenyl,  
 15 phenylalkyl, alkoxyphenyl or alkylphenyl.

7. Composite material of claim 7 wherein:

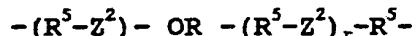
R<sub>1</sub> is alkyl of from 1 to 4 carbon atoms; and

-R<sup>2</sup>- is a moiety of the formula:



20 wherein:

-R<sup>3</sup>- is a divalent substituted or unsubstituted alkylenephenylene, alkylenephenylenealkylene or a divalent moiety selected from the group consisting of:



25 wherein:

R<sup>5</sup> is the same or different at each occurrence and are substituted or unsubstituted and are alkylene or phenylene; and

r is an integer equal to or greater than 1;

30 wherein permissible substituents are one or more hydroxy, cyano, or alkoxy or alkyl having from 1 to about 4 carbon atoms;

-Z<sup>1</sup> is -CH<sub>2</sub>-, -NH-, -O-, -C(O)-, -S-, -S<sub>2</sub>-, -S<sub>3</sub>-, -S<sub>4</sub>-, -N(H)C(O)- or -C(O)N(H); and

- 45 -

-Z<sup>2</sup>- is -O-, -NH-, -OC(O)-, -N(H)C(O)-, -C(O)-, or -N(H)C(O)N(H)-.

8. Composite material of claim 6 wherein said polymeric matrix comprises a polyamide, a polyester, halogenated polyolefin, a polyolefin, a polyvinyl or a combination thereof.

9. Composite material of claim 8 wherein said polymeric matrix comprises a polyester, a polyamide, a polyolefin or a halogenated polyolefin, with the proviso that; when said matrix comprises a polyester, -Z<sup>1</sup>- is selected from the group consisting of -NH-, -N(H)C(O)- and -O-; when said polymeric matrix comprises a polyolefin, a halogenated polyolefin or a combination thereof, -Z<sup>1</sup>- is selected from the group consisting of -O-, -NH-, -CH<sub>2</sub>-, -S- or -S<sub>n</sub>-; and when said polymeric matrix comprises a polyamide, -Z<sup>1</sup>- is -N(H)-, -O- or -N(H)C(O)N(H)-

10. A process for forming a polymeric composite which comprises platelet particles dispersed in a polymeric matrix, said process comprising the steps of:

(a) forming a flowable mixture comprising a polymer melt and a swellable and polymer-compatible intercalated layered material wherein an organo silane species is bonded to the surface of the layers of said material, said species having at least one functional group which is reactive with at least one polymeric species in said matrix to form a covalent bond; and

(b) subjecting said mixture to a shear having a shear rate which is sufficient to dissociate all or a portion of said layers to form platelet particles having an average thickness of less than about 50 Å and to uniformly disperse said platelet particles in said polymer to form said polymer composite wherein said platelet particles are uniformly

- 46 -

dispersed in said matrix and wherein said organo  
silane species reacts with said component forming  
an organo silane residue which is covalently bonded  
to the surfaces of said particles and said  
5 component.



## INTERNATIONAL SEARCH REPORT

PCT/US 92/10098

International Application No

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C08K7/00; //C08K3/34C08K9/06		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl. 5	C08K ; C08L	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	EP,A,0 099 710 (STANDARD OIL COMPANY) 1 February 1984 see page 3, line 23 - page 6, line 10 see page 7, line 27 - page 9, line 24; claims ---	1-7
A	US,A,3 915 735 (JAMES E. MORELAND) 28 October 1975 see column 4, line 66 - column 5, line 15; claims ---	1,10
A	CHEMICAL ABSTRACTS, vol. 97, no. 22, 29 November 1982, Columbus, Ohio, US; abstract no. 183445u, see abstract & JP,A,57 090 050 (TOYOTA CENTRAL RESEARCH AND DEVELOPMENT LABORATORIES, INC.) 4 June 1982 --- -/-	1
<sup>10</sup> Special categories of cited documents : <sup>10</sup> <sup>"A"</sup> document defining the general state of the art which is not considered to be of particular relevance <sup>"E"</sup> earlier document but published on or after the international filing date <sup>"I"</sup> document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) <sup>"O"</sup> document referring to an oral disclosure, use, exhibition or other means <sup>"P"</sup> document published prior to the international filing date but later than the priority date claimed <sup>"T"</sup> later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention <sup>"X"</sup> document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step <sup>"Y"</sup> document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. <sup>"&amp;"</sup> document member of the same patent family		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
03 MARCH 1993	22. 03. 93	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	de Los Arcos, E.	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claims No.
A	EP,A,0 398 551 (UBE INDUSTRIES, LTD.) 22 November 1990 cited in the application see claims -----	1

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9210098  
SA 67446

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

03/03/93

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0099710	01-02-84	US-A- 4431755	14-02-84
		CA-A- 1220296	07-04-87
		JP-A- 59027933	14-02-84
-----			
US-A-3915735	28-10-75	None	
-----			
EP-A-0398551	22-11-90	JP-A- 2305828	19-12-90
		US-A- 5102948	07-04-92
-----			

EPO FORM P079

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

